Reactions of the Chloro(diisopropylamino)phosphanylium Cation with Unsaturated Alcohols

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The chloro(diisopropylamino)phosphanylium cation $[(Pr^i_2N)(Cl)P]^+[AlCl_4]^-$ **1** reacts with prop-2-ynyl alcohols **2a–d** to give prop-2-ynyl aminophosphonic chlorides **3a–d** in good yield. Using cinnamyl alcohol and benzyl alcohol instead of **2a–d**, the reactions of cation **1** afforded the corresponding aminophosphonic chlorides. In the reaction of cation **1** with ethanol, however, no aminophosphonic chloride **8** could be isolated. The yields of these reactions were better when two equivalents of cation **1** were used. The reaction mechanisms are also discussed.

Phosphanylium cations are isoelectronic with singlet state carbenes and silylenes, having a reactive phosphorus group with a lone pair of electrons and a vacant 3p orbital, and act as strong Lewis acids.[1,2] Furthermore, they react with unsaturated organic molecules to afford various phosphorus-containing heterocycles which are well documented,[3] however references regarding the reaction of phosphanylium cations with unsaturated compounds having a hetero atom are few in number.[4] In the present paper, the reactions of chloro(diisopropylamino)phosphanylium cations with compounds having two active sites such as prop-2-ynyl alcohols and allyl alcohols are described.

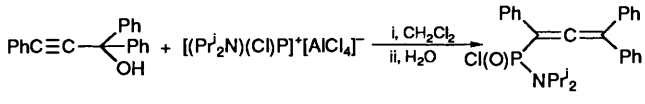
Results and Discussion

4-Phenylbut-3-yn-2-ol **2a** reacted with 2 equiv. of chloro(diisopropylamino)phosphanylium cation at −78 °C over 1 h to give *N,N*-diisopropyl-*P*-(4-phenylbut-3-yn-2-yl)phosphonamidic chloride **3a** in 61% yield as a diastereoisomeric mixture which was separated by column chromatography on silica gel. The structure of each diastereoisomer, established on the basis of spectral evidence and the results of elemental analysis, was confirmed by X-ray crystallography (Fig. 1 and Experimental section). When equimolar amounts of phosphanylium cation were used in the reaction with alcohol **2a**, the yield of phosphonamidic chloride **3a** was poor (30%; entry 1 in Table 1).

It is well known that prop-2-ynyl alcohols react with phosphorus halides to form alk-2-ynyl trivalent phosphorus esters which isomerize to allenyloxo-λ^5-phosphanes *via* a concerted [2,3] sigmatropic rearrangement.[5] In the present study, however, these allenyl phosphorus compounds were not obtained, except in the reaction with 1,1,3-triphenylprop-2-ynol **2e** (*vide infra*).

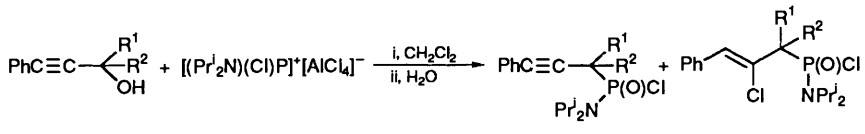
The reaction of phosphanylium cation **1** with 1,3-diphenylprop-2-ynol **2b** yielded two major products (43 and 45%, respectively; entry 4). One product was alkyne compound **3b** (yield 45%), which showed an alkyne band at 1950 cm^{-1} in its IR spectrum. The mass spectrum of the other product **4b** showed a molecular ion peak at *m/z* 410 (M^+) and 412 (M + 2). Furthermore, the IR spectrum showed an alkene band at 1630 cm^{-1} and no peak was observed at 1950 cm^{-1}. NMR spectroscopy and elemental analysis suggested that this product was *N,N*-diisopropyl-*P*-(2-chloro-1,3-diphenylprop-2-enyl)phosphonamidic chloride **4b**. In this case a stoichiometric reaction of phosphanylium cation **1** and alcohol **2b** also resulted in a poor yield of phosphonamidic chloride **4b** (entry 3).

As shown in Table 1, the phosphanylium salt **1** provided the corresponding aminophosphonic chloride from the reactions of various prop-2-ynyl alcohols under similar conditions. However, the reaction of alcohol **2e** with 2 equiv. of phosphanylium



2e **1** **5**

Table 1 The reactions of chloro(diisopropylamino)phosphanylium cations with prop-2-ynyl alcohol derivatives

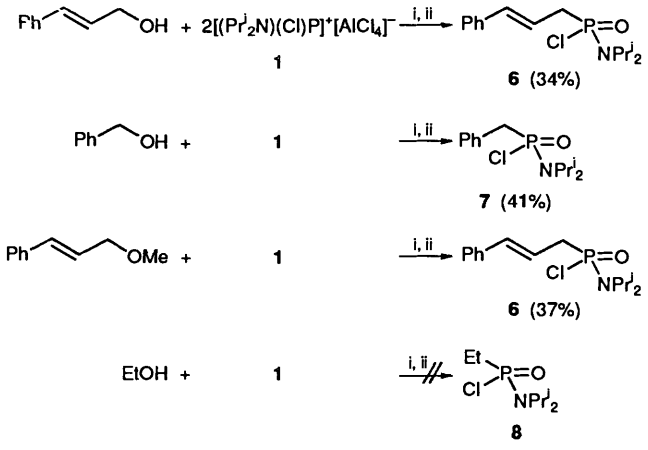


2a–d **1** **3a–d** **4b**

Entry	Substrate	R^1	R^2	Ratio of **2**:**1**	Product (yield, %)
1	**2a**	Me	H	1:1	**3a** (30)
2	**2a**	Me	H	1:2	**3a** (61)[a]
3	**2b**	Ph	H	1:1	**4b** (6)
4	**2b**	Ph	H	1:2	**3b** (45),[b] **4b** (43)
5	**2c**	Me	Me	1:2	**3c** (87)
6	**2d**	$-[CH_2]_5-$		1:2	**3d** (88)

[a] Diastereoisomers (*S*,S**)- and (*S*,R**)-**3a** were isolated in 59 and 2% yield, respectively. [b] Product **3b** was isolated as a diastereoisomeric mixture. The ratio of (*S*,S**):(*S*,R**) was about 2:1 which was estimated from the doublet signals of the methyne protons in the NMR.

cation **1** gave allenylaminophosphonic chloride **5** in 93% yield. The product **5** showed an allenic stretching band at 1910 cm^{-1} in its IR spectrum and the ^{13}C NMR spectrum showed resonances for allenic carbons at δ 103.3, 110.6 and 212.8. The reaction of phosphanylium cation **1** with cinnamyl alcohol and benzyl alcohol yielded the corresponding aminophosphonic chlorides **6** and **7** in 34 and 41% yield, respectively. Furthermore, the cation **1** reacted with cinnamyl methyl ether to give



Reagents: i, CH_2Cl_2; ii, H_2O

the phosphonic chloride **6** in 37% yield, but the reaction with ethanol did not yield compound **8**.

Based on the above results, a plausible mechanism can be postulated to explain the formation of aminophosphonic chlorides **3a–d**, **7** and **9** (Scheme 1).

In the first stage, the nucleophilic attack of the oxygen onto the phosphanylium cation forms the adduct **9**, which is converted by chloride ion and/or tetrachloroaluminate into phosphane **10** along with an elimination of hydrogen chloride or methyl chloride. To clarify the formation of alkyl chloride, we

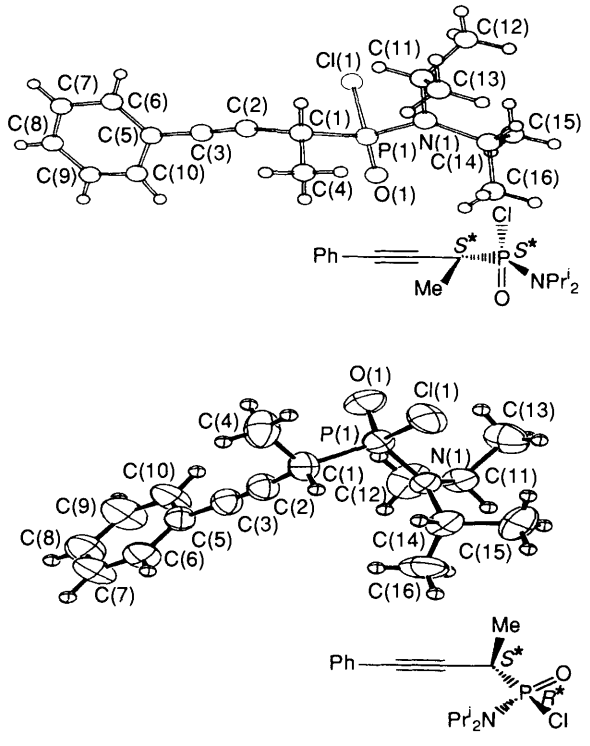
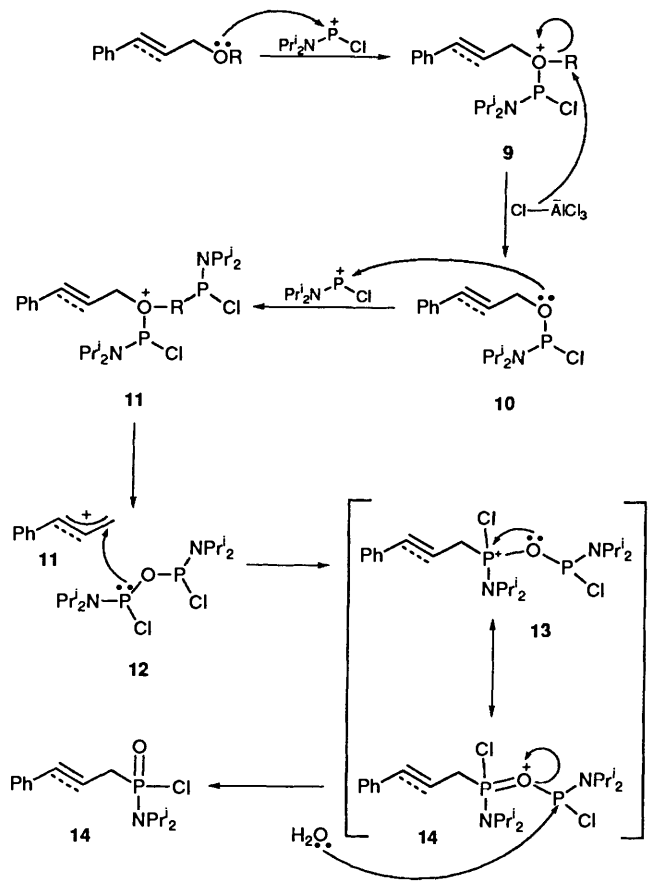


Fig. 1 Crystal structures of (*a*) (*S**,*S**)-**3a** and (*b*) (*S**,*R**)-**3a**

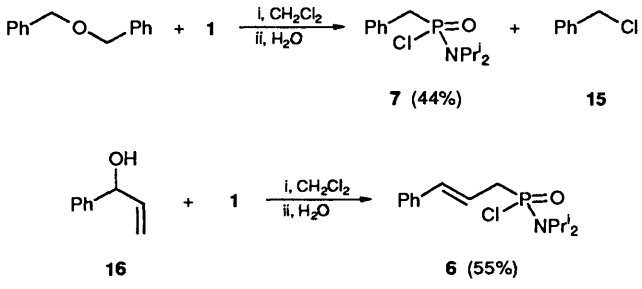


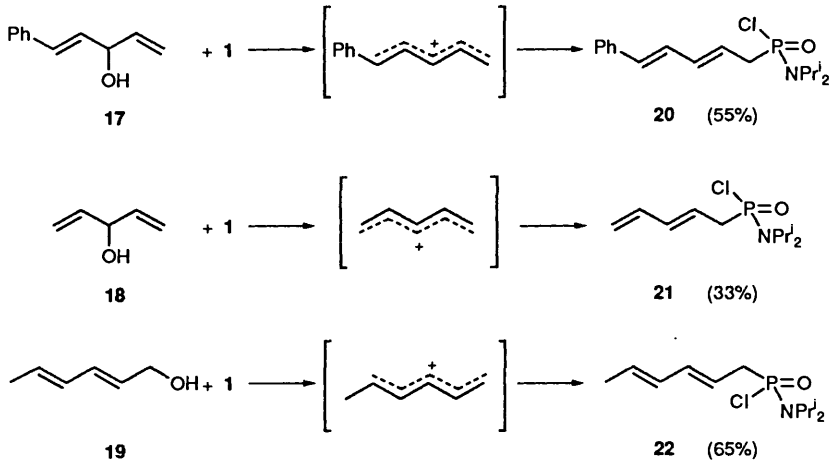
Scheme 1 Reaction mechanism of chloro(diisopropylamino)phosphanylium cation with unsaturated alcohol

attempted the reaction of cation **1** with dibenzyl ether, which under the same conditions gave the expected aminophosphonic chloride **7** in 44% yield, whilst benzyl chloride **15** was detected by gas chromatography.

In the second step, the intermediate **10** attacks a further molecule of phosphanylium cation to form adduct **11**, which is followed by carbon–oxygen bond cleavage resulting in a stable carbocation **12** and diphosphane **13**. Because of the high reactivity of the phosphanylium cation, an intramolecular rearrangement of the intermediate **10** could not occur. Furthermore, the fact that the reactions required 2 equiv. of phosphanylium cations is explained by the above mechanism. In the reaction of cation **1** with ethanol, a stable carbocation cannot be generated. Furthermore, the reaction of 2 equiv. of cation **1** with 1-phenylprop-2-enol **16**, which would give the same carbocation as that in the reaction with cinnamyl alcohol and cinnamyl methyl ether, gave aminophosphonic chloride **6** in 55% yield.

An alternative mechanism might be an Arbuzov route *via* intermediate **10**. This route, however, can be excluded since it

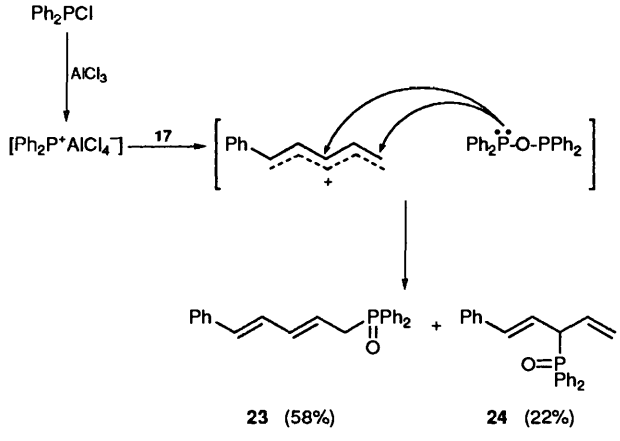




would require only an equimolar amount of the phosphanylium cation.

The carbocation **12** can then accept nucleophilic attack by the trivalent phosphorus atom to give intermediate **13**. In the case of the reaction of 1,1,3-triphenylprop-2-ynol, the less steric hindered carbon would be attacked to form allenylaminophosphonic chloride **5**. Finally, the aminophosphonic chloride is formed by the addition of water.

Reactions of cation **1** with 1-phenylpenta-1,4-dien-3-ol **17**, penta-1,4-dien-3-ol **18** and hexa-2,4-dienol **19** did not give Nazarov products but dienylaminophosphonic chlorides **20**–**22** in 55, 33 and 65% yield, respectively. These reactions would also proceed *via* stable pentadienyl cations. Furthermore, the reaction of alcohol **17** with chlorodiphenylphosphane in the presence of aluminium chloride gave oxo-λ^5-phosphanes **23** and **24** in 58 and 22% yield, respectively.



Experimental

Melting points were taken with a Yanagimoto micro melting point apparatus. IR spectra were obtained on a JASCO A-100 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL FX-90 and JEOL α-400 spectrometers. All chemical shifts are reported in (δ) ppm from tetramethylsilane and coupling constants are given in Hz. Mass spectra were taken with a Hitachi M-80B spectrometer. Analytical gas chromatography was performed on a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector. The column used was an OV-7 stainless steel column: the injector temperature was 100 °C, the column temperature was 80 °C, and hydrogen gas and air 0.5 kg cm^{-2} and nitrogen gas 0.25 kg cm^{-2} were used. Retention times and peak integrals were obtained from a Shimadzu C-R6A recorder.

Synthesis of N,N-*Diisopropyl*-P-(4-*phenylbut*-3-*yn*-2-*yl*)*phosphonamidic Chloride* **3a**.—A solution of dichloro(diisopropylamino)phosphine (2.76 g, 13.68 mmol) in anhydrous dichloromethane (15 cm^3) was added to a stirred solution of aluminium chloride (anhydrous; 1.82 g, 13.68 mmol) in anhydrous dichloromethane (15 cm^3) under nitrogen at −78 °C. The mixture was allowed to warm to room temperature over 1 h and then cooled to −78 °C again. A solution of 4-phenylbut-3-yn-2-ol (1.00 g, 6.84 mmol) in anhydrous dichloromethane (15 cm^3) was added to the mixture which was then stirred for an additional 1 h at −78 °C. The mixture was allowed to warm to room temperature and then quenched with water (20 cm^3). The mixture was extracted with dichloromethane (30 cm^3 × 3) and the extract washed with brine (30 cm^3) and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel eluting with EtOAc–hexane (0:1–1:3) to give a solid which was recrystallized from hexane to give the title compounds (*S**,*S**)- and (*S**,*R**)-**3a** as colourless crystalline solids in 59% (1.25 g, 4.01 mmol) and 2% (0.05 g, 0.16 mmol) yields, respectively.

(*S**,*S**)-**3a**: M.p. 104–105 °C (Found: C, 61.6; H, 7.4; N, 4.4. $C_{16}H_{23}ClNOP$ requires C, 61.6; H, 7.4; N, 4.5%); ν_{max}(KBr)/cm^{-1} 2970, 2930, 2855 (CH), 2210 (C≡C), 1600, 1495, 1440, 1400, 1360 (CH_3), 750, 720 and 680 [CH(Ph)]; δ_H(90 MHz; $CDCl_3$) 1.31 (6 H, d, *J* 4.4, NCCH_3), 1.38 (6 H, d, *J* 4.4, NCCH_3), 3.15–3.87 (3 H, m, NCH and CH) and 7.24–7.49 (5 H, m, Ph); δ_C(22.63 MHz; $CDCl_3$) 16.3 (d, $^2J_{PC}$ 4.9, PCCH_3), 21.9 (d, $^3J_{PC}$ 2.0, NCCH_3), 22.7 (d, $^3J_{PC}$ 3.9, NCCH_3), 35.5 (d, $^1J_{PC}$ 120.6, PCH), 48.1 (d, $^2J_{PC}$ 2.4, NCH), 85.7 (d, $^3J_{PC}$ 11.7, *C*≡C), 123.0 (d, $^2J_{PC}$ 4.4, C≡*C*) and 128.3–131.8 (ArCs); *m*/*z* 296 ($M^+ - CH_3$).

(*S**,*R**)-**3a**: M.p. 69–70 °C (Found: C, 61.6; H, 7.4; N, 4.4. $C_{16}H_{23}ClNOP$ requires C, 61.6; H, 7.4; N, 4.5%); ν_{max}(KBr)/cm^{-1} 2950, 2940, 2870 (CH), 2220 (C≡C), 1590, 1480, 1440, 1400, 1360 (CH_3), 745, 720 and 680 [CH(Ph)]; δ_H(90 MHz; $CDCl_3$) 1.38 (12 H, d, *J* 5.4, NCCH_3), 1.68 (3 H, dd, *J* 7.0, 20.78, PCCH_3), 3.32–3.71 (3 H, m, NCH and CH) and 7.25–7.40 (5 H, m, Ph); δ_C(22.63 MHz; $CDCl_3$) 15.0 (d, $^2J_{PC}$ 4.4, PCCH_3), 21.6 (d, $^3J_{PC}$ 2.0, NCCH_3), 22.6 (d, $^3J_{PC}$ 3.9, NCCH_3), 34.0 (d, $^1J_{PC}$ 121.1, PCH), 47.7 (d, $^2J_{PC}$ 2.9, NCH), 85.5 (d, $^3J_{PC}$ 12.7, *C*≡C), 123.0 (d, $^2J_{PC}$ 4.9, C≡*C*) and 128.4–131.7 (ArCs).

N,N-*Diisopropyl*-P-(1,3-*diphenylprop*-2-*yn*-1-*yl*)*phosphonamidic Chloride* **3b** *and* N,N-*Diisopropyl*-P-(2-*chloro*-1,3-*diphenylprop*-2-*enyl*)*phosphonamidic Chloride* **4b**.—In the same way, dichloro(diisopropylamino)phosphine (1.94 g, 9.60 mmol), aluminium chloride (anhydrous; 1.28 g, 9.60 mmol) and 1,3-diphenylprop-2-ynol (1.00 g, 4.80 mmol) gave the title compounds **3b** (0.81 g, 2.17 mmol, 45%) and **4b** (0.85 g, 2.07 mmol, 43%), respectively. **3b** As a colourless crystalline solid,

m.p. 109–110 °C (Found: C, 67.6; H, 6.9; N, 3.6. $C_{21}H_{25}ClNOP$ requires C, 67.5; H, 6.7; N, 3.75%); ν_{max}(KBr)/cm^{-1} 3070, 3040 [CH(Ph)], 2970, 2945, 2920 (CH), 1950 (C≡C), 1600, 1495, 1450, 1385, 1370 (CH_3), 1240 (P=O), 755 and 690 [CH(Ph)]; δ_H(90 MHz; $CDCl_3$) 1.06 (6 H, d, *J* 6.4, NCCH_3), 1.32 (6 H, d, *J* 7.0, NCCH_3), 3.20–4.00 (2 H, m, NCH), 4.57 (0.64 H, d, *J* 22.6, PCH), 4.69 (0.36 H, d, *J* 23.7, PCH) and 7.17–7.72 (10 H, m, Ph); δ_C(22.63 MHz; $CDCl_3$) 21.7 (d, $^3J_{PC}$ 2.5, NC*C*H_3), 22.0 (d, $^3J_{PC}$ 2.0, NC*C*H_3), 22.3 (d, $^3J_{PC}$ 3.9, NC*C*H_3), 22.6 (d, $^3J_{PC}$ 3.4, NC*C*H_3), 46.8 (d, $^1J_{PC}$ 113.3, PCH), 48.0 (d, $^1J_{PC}$ 113.8, PCH), 47.9 (d, $^2J_{PC}$ 2.4, NCH), 48.2 (d, $^2J_{PC}$ 2.4, NCH), 84.2 (d, $^3J_{PC}$ 13.2, *C*≡C), 123.0 (d, $^2J_{PC}$ 4.9, C≡*C*) and 128.1–131.9 (ArCs); *m*/*z* 373 (M^+).

4b As a colourless crystalline solid, m.p. 185–186 °C (Found: C, 61.5; H, 6.4; N, 3.3. $C_{21}H_{26}Cl_2NOP$ requires C, 61.7; H, 6.4; N, 3.1%); ν_{max}(KBr)/cm^{-1} 3030 [CH(Ph)], 2975, 2925, 2875 (CH), 1630 (C=C), 1600, 1495, 1450, 1400, 1370 (CH_3), 1235 (P=O), 750 and 680 [CH(Ph)]; δ_H(90 MHz; $CDCl_3$) 0.87 (6 H, d, *J* 6.4, NCCH_3), 1.35 (6 H, d, *J* 6.6, NCCH_3), 3.20–3.59 (2 H, m, NCH), 4.38 (1 H, d, *J* 19.8, PhCH=C) and 7.25–7.68 (11 H, m, Ph and olefin Hs); δ_C(22.63 MHz; $CDCl_3$) 21.8 (d, $^3J_{PC}$ 2.0, NC*C*H), 22.1 (d, $^3J_{PC}$ 4.4, NC*C*H), 48.1 (d, $^2J_{PC}$ 2.4, NCH), 62.2 (d, $^1J_{PC}$ 112.8, PCH) and 128.1–130.6 (ArCs); *m*/*z* 410 (M^+).

N,N-*Diisopropyl*-P-(2-*methyl*-4-*phenylbut*-3-*yn*-2-*yl*)*phosphonamidic Chloride* **3c**.—In the same way, dichloro(diisopropylamino)phosphine (2.52 g, 12.50 mmol), aluminium chloride (anhydrous; 1.67 g, 12.50 mmol) and 2-methyl-4-phenylbut-3-yn-2-ol (1.00 g, 6.24 mmol) gave the title compound **3c** (1.77 g, 5.43 mmol, 87%) as a colourless crystalline solid, m.p. 69–70 °C (Found: C, 62.4; H, 7.7; N, 4.5. $C_{17}H_{25}ClNOP$ requires C, 62.7; H, 7.7; N, 4.3%); ν_{max}(KBr)/cm^{-1} 3070 [CH(Ph)], 2975, 2940, 2875 (CH), 1950 (C≡C), 1740, 1600, 1490, 1450, 1400, 1380, 1365 (CH_3), 1240 (P=O), 755, 720 and 680 [CH(Ph)]; δ_H(90 MHz; $CDCl_3$) 1.29 (6 H, d, *J* 6.6, NCCH_3), 1.33 (6 H, d, *J* 6.6, NCCH_3), 1.66 (3 H, d, *J* 19, PCCH_3), 3.51–4.18 (2 H, m, NCH) and 7.33–7.73 (5 H, m, Ph); δ_C(22.63 MHz; $CDCl_3$) 21.9 (d, $^3J_{PC}$ 2.0, NC*C*H), 22.7 (d, $^3J_{PC}$ 3.9, NC*C*H), 24.5 (d, $^2J_{PC}$ 2.0, PC*C*H_3), 26.0 (d, $^2J_{PC}$ 2.0, PC*C*H_3), 40.3 [d, $^1J_{PC}$ 120.1, P*C*$(CH_3)_2$], 48.5 (d, $^2J_{PC}$ 2.0, NCH), 83.9 (d, $^3J_{PC}$ 10.7, *C*≡C), 123.0 (d, $^2J_{PC}$ 3.9, C≡*C*) and 128.4–131.5 (ArCs); *m*/*z* 325 (M^+).

N,N-*Diisopropyl*-P-[1-(2-*phenylethynyl*)*cyclohexyl*]*phosphonamidic Chloride* **3d**.—In the same way, dichloro(diisopropylamino)phosphine (2.52 g, 9.98 mmol), aluminium chloride (anhydrous; 1.33 g, 9.98 mmol) and 1-(2-phenylethynyl)cyclohexanol (1.00 g, 4.99 mmol) gave the title compound **3d** (1.61 g, 4.40 mmol, 88%) as a colourless crystalline solid, m.p. 77–78 °C (Found: C, 65.8; H, 7.95; N, 3.9. $C_{20}H_{29}CNOP$ requires C, 65.7; H, 8.0; N, 3.8%); ν_{max}(KBr)/cm^{-1} 3070 [CH(Ph)], 2975, 2940, 2875 (CH), 1950 (C≡C), 1740, 1600, 1490, 1450, 1400, 1380, 1365 (CH_3), 1240 (P=O), 755 and 680 [CH(Ph)]; δ_H(90 MHz; $CDCl_3$) 1.30 (6 H, d, *J* 4.8, NCCH_3), 1.37 (6 H, d, *J* 4.8, NCCH_3), 1.50–2.20 (10 H, m, –[CH_2]$_5$–), 3.67–4.20 (2 H, m, NCH) and 7.26–7.43 (5 H, m, Ph); δ_C(22.63 MHz; $CDCl_3$) 22.0 (d, $^3J_{PC}$ 2.0, NC*C*H), 22.3 (d, $^3J_{PC}$ 3.9, cyclohexyl-2C), 22.8 (d, $^3J_{PC}$ 3.4, NC*C*H), 23.0 (s, cyclohexyl-4C), 25.3 (d, $^3J_{PC}$ 2.0, cyclohexyl-2C), 31.4 (d, $^2J_{PC}$ 3.4, PC*C*), 32.3 (d, $^2J_{PC}$ 2.9, PC*C*), 46.7 (d, $^1J_{PC}$ 121.1, PC), 48.4 (d, $^2J_{PC}$ 1.5, NCH), 86.9 (d, $^3J_{PC}$ 11.7, *C*≡C), 123.2 (d, $^2J_{PC}$ 3.9, C≡*C*) and 128.3–131.5 (ArCs); *m*/*z* 350 ($M^+ - CH_3$).

N,N-*Diisopropyl*-P-(1,3,3-*triphenylpropa*-1,2-*dienyl*)*phosphonamidic Chloride* **5**. In the same way, dichloro(diisopropylamino)phosphine (1.42 g, 7.04 mmol), aluminium chloride (anhydrous; 0.94 g, 7.04 mmol), and 1,1,3-triphenylprop-2-ynol (1.00 g, 3.52 mmol) gave the title compound **5** (1.48 g, 3.29 mmol, 93%) as a colourless crystalline solid, m.p. 185–186 °C (Found: C, 72.2; H, 6.6; N, 3.2. $C_{27}H_{29}ClNOP$ requires C, 72.1; H, 6.5; N, 3.1%); ν_{max}(KBr)/cm^{-1} 3050 [CH(Ph)], 3025, 2975, 2940, 2875 (CH), 1910, 1600, 1490, 1440, 1400, 1380, 1365 (CH_3), 1240 (P=O), 755 and 680 [CH(Ph)]; δ_H(90 MHz; $CDCl_3$) 0.97 (6 H, d, *J* 6.6, NCCH_3), 1.27 (6 H, d, *J* 6.7, NCCH_3), 3.16–3.60 (2 H, m, NCH) and 7.35–7.76 (15 H, m, Ph); δ_C(22.63 MHz; $CDCl_3$) 21.2 (d, $^3J_{PC}$ 2.9, NC*C*H), 22.5 (d, $^3J_{PC}$ 4.4, NC*C*H), 47.8 (d, $^2J_{PC}$ 4.0, NCH), 107.6 [d, $^1J_{PC}$ 164.5, P*C*(Ph)], 128.4–128.8 (ArCs) and 212.8 (d, $^2J_{PC}$ 4.0, allenic-C); *m*/*z* 449 (M^+).

N,N-*Diisopropyl*-P-(3-*phenylprop*-2-*enyl*)*phosphonamidic Chloride* **6**.—In the same way, dichloro(diisopropylamino)-phosphine (3.01 g, 14.9 mmol), aluminium chloride (anhydrous; 1.99 g, 14.9 mmol), and cinnamyl alcohol (1.00 g, 7.45 mmol) gave the title compound **6** (0.76 g, 2.5 mmol, 34%) as a colourless crystalline solid, m.p. 86–87 °C (Found: C, 60.1; H, 7.7; N, 4.8. $C_{15}H_{23}ClNOP$ requires C, 60.1; H, 7.7; N, 4.7%); ν_{max}(KBr)/cm^{-1} 3090, 3040 [CH(Ph or olefin)], 3000, 2940, 2870, 1600, 1500, 1450, 1245 (P=O), 1000, 970 [CH(CH=CH)], 730 and 695 [CH(Ph)]; δ_H(90 MHz; $CDCl_3$] 1.27 (6 H, d, *J* 6.8, NCCH_3), 1.37 (6 H, d, *J* 7.0, NCCH_3), 3.01–3.68 (4 H, m, PCH_2, NCH), 6.08–6.72 (2 H, m, PCCH, PhCH) and 7.27–7.33 (5 H, m, Ph); δ_C(22.63 MHz; $CDCl_3$) 21.5 (d, $^3J_{PC}$ 2.9, NC*C*H), 22.9 (d, $^3J_{PC}$ 3.9, NC*C*H), 41.6 (d, $^1J_{PC}$ 116, PCH_2), 47.6 (d, $^2J_{PC}$ 3.4, NCH) and 118.1–136.5 (ArCs); *m*/*z* 299 (M^+).

Compound **6** was also obtained from the reactions of 3-phenyl-1-methoxyprop-2-enol (1.00 g, 6.75 mmol) with dichloro(diisopropylamino)phosphine (2.73 g, 13.5 mmol) and aluminium chloride (anhydrous; 1.80 g, 13.5 mmol) and 1-phenylprop-2-enol (1.00 g, 7.45 mmol) with dichloro(diisopropylamino)phosphine (2.76 g, 13.68 mmol) and aluminium chloride (anhydrous; 1.82 g, 13.68 mmol) in 37% (0.74 g, 2.47 mmol) and 55% (1.22 g, 4.07 mmol) yield, respectively.

N,N-*Diisopropyl*-P-(5-*phenylpenta*-2,4-*dienyl*)*phosphonamidic Chloride* **20**.—In the same way, dichloro(diisopropylamino)phosphine (1.57 g, 7.74 mmol), aluminium chloride (anhydrous; 1.04 g, 7.74 mmol) and 1-phenylpenta-1,4-dien-3-ol (0.62 g, 3.87 mmol) gave the title compound **20** (0.70 g, 2.15 mmol, 56%) as a colourless crystalline solid, m.p. 104–105 °C (Found: C, 62.9; H, 7.8; N, 4.2. $C_{17}H_{25}ClNOP$ requires C, 62.7; H, 7.7; N, 4.3%); ν_{max}(KBr)/cm^{-1} 2975, 1250 (P=O), 1180, 1160, 1025, 750 and 680; δ_H(90 MHz; $CDCl_3$) 1.32 (12 H, dd, *J* 6.8, CH_3), 2.94–3.67 (4 H, m, CH, CH_2), 5.84 (1 H, m, *J* 7.7), 6.41–6.74 (3 H, m) and 7.40–7.23 (5 H, m, Ph); δ_C(22.63 MHz; $CDCl_3$) 22.1 (d, $^3J_{PC}$ 31.1, NCCH_3), 22.2 (d, $^3J_{PC}$ 32.4, NCCH_3), 41.4 (d, $^1J_{PC}$ 116.0, P*C*C), 47.5 (d, $^2J_{PC}$ 3.1, N*C*CH_3), 121.7–137.1 [ArCs and –CH_2=CH– (121.7, J_{PC} 13.4)], 126.4, 126.5, 127.7, 127.9, 128.1, 128.6, 132.9 (J_{PC} 5.5), 136.25, 137.0 and 137.1); *m*/*z* 325 (M^+).

N,N-*Diisopropyl*-P-*penta*-2,4-*dienylphosphonamidic Chloride* **21**.—In the same way, dichloro(diisopropylamino)phosphine (2.40 g, 11.89 mmol), aluminium chloride (anhydrous; 1.59 g, 11.89 mmol), and penta-1,4-dien-3-ol (0.50 g, 5.94 mmol) gave the title compound **21** (0.49 g, 1.96 mmol, 33%) as a pure yellow syrup; ν_{max}(KBr)/cm^{-1} 3100 (=CH_2), 3000, 2950 (CH), 2900, 1600, 1460, 1410 (CH_2=CH), 1370 [CH$(CH_3)_2$], 1250 (P=O), 1210, 1180, 1160, 1130 [CH$(CH_3)_2$], 1000, 900, 810 and 750; δ_H(400 MHz; $CDCl_3$) 1.25 (6 H, d, *J* 6.8, CH_3), 1.35 (6 H, d, *J* 6.8, CH_3), 3.02 (2 H, m, CH_2), 3.46 (2 H, m, *J* 6.8, CH_3), 5.10 (1 H, d, *J* 10.5, CH_2=CHCH=CH), 5.20 (1 H, d, *J* 16.1, CH_2=CHCH=CH), 5.75–5.65 (1 H, *J* 7.6, t, *J* 7.6, d, *J* 15.0, d, CH_2=CHCH=C*H*) and 6.38–6.20 (2 H, m, CH_2=C*H*C*H*=CH);

δ_C(22.63 MHz; $CDCl_3$) 22.2 (d, $^3J_{PC}$ 30.3, CH_3), 22.2 (d, $^3J_{PC}$ 29.3, CH_3), 41.2 (d, $^1J_{PC}$ 116.2, PCC), 47.6 (d, $^2J_{PC}$ 2.9, NCCH$_3$), 117.5 (d, $^5J_{PC}$ 4.9, PCC=CC=C), 121.9 (d, $^2J_{PC}$ 13.2, PCC=C), 136.1 (d, $^4J_{PC}$ 5.4, PCC=CC=C) and 137.0 (d, $^3J_{PC}$ 17.1, PCC=CC=C); *m/z* 249 (M^+) (Found: M^+, 249.1060. $C_{11}H_{21}ClNOP$ requires M^+, 249.1048).

N,N-*Diisopropyl*-P-*hexa*-2,4-*dienylphosphonamidic Chloride* **22**.—In the same way, dichloro(diisopropylamino)phosphine (3.02 g, 10.0 mmol), aluminium chloride (anhydrous; 1.33 g, 10.0 mmol) and hexa-2,4-dienol (0.49 g, 5.00 mmol) gave the title compound **22** (0.90 g, 3.25 mmol, 65%) as a colourless syrup; ν_{max}(KBr)/cm^{-1} 2970, 2940, 1660 (CH=CH), 1450, 1410, 1370 [CH(CH$_3$)$_2$], 1250 (P=O), 1200, 1180, 1160, 1110 [CH(CH$_3$)$_2$], 990, 920, 880, 820 and 730; δ_H(90 MHz; $CDCl_3$) 1.10 (6 H, d, *J* 6.9, NCCH$_3$), 1.20 (6 H, d, *J* 6.7, NCCH$_3$), 1.65–1.54 (3 H, m, CH_3), 2.74 (1 H, d, *J* 7.4, CH_2), 2.98 (1 H, d, *J* 7.4, CH_2), 3.11–3.50 (2 H, m, NC*H*CH$_3$) and 5.41–5.99 (4 H, m, C*H*=C*H*); δ_C(22.63 MHz; $CDCl_3$) 22.2 (d, $^3J_{PC}$ 29.1, NCCH$_3$), 22.3 (d, $^3J_{PC}$ 30.2, NCCH$_3$), 41.5 (d, $^1J_{PC}$ 115.9, PCC=C), 47.7 (d, $^2J_{PC}$ 3.3, NCCH$_3$), 118.6 (d, $^2J_{PC}$ 13.2, PCC=C), 129.8 (d, $^5J_{PC}$ 4.9, PCC=CC=C), 131.0 (d, $^4J_{PC}$ 5.0, PCC=CC=C) and 136.6 (d, $^3J_{PC}$ 17.0, PCC=C); *m/z* 263 (M^+) (Found: M^+, 263.1241. $C_{12}H_{23}ClNOP$ requires M^+, 263.1205).

Oxodiphenyl(5-*phenylpenta*-2,4-*dienyl*)-λ^5-*phosphane* **23** *and Oxodiphenyl*(1-*phenylpenta*-1,4-*dien*-3-*yl*)-λ^5-*phosphane* **24**.—In the same way, chlorodiphenylphosphine (1.33 g, 6.0 mmol), aluminium chloride (anhydrous; 0.8 g, 6.0 mmol) and 1-phenylpenta-1,4-dien-3-ol (0.48 g, 3.0 mmol) gave the title compounds **23** (0.60 g, 1.74 mmol, 58%) and **24** (0.23 g, 0.66 mmol, 22%), respectively. Compound **23** as a colourless crystalline solid, m.p. 217 °C (Found: C, 79.85; H, 6.2. $C_{23}H_{21}OP$ requires C, 80.2; H, 6.15%); ν_{max}(KBr)/cm^{-1} 3030, 1590, 1480, 1440, 1300, 1180, 1100, 980, 840, 740, 720 and 680; δ_H(90 MHz; $CDCl_3$) 3.22 (2 H, dd, *J* 7.5, 7.3 CH_2), 6.47–6.56 (4 H, m, CH=CH) and 7.24–7.87 (15 H, m, ArH); δ_C(22.63 MHz; $CDCl_3$) 35.6 (d, $^1J_{PC}$ 68.4, CH_2) and 122.0–136.4 [ArCs and CH=CH (122.0, 122.4, 126.4, 127.5, 128.2, 128.4, 128.4, 128.6, 128.9, 130.9, 131.3, 131.8, 131.9, 132.1, 135.9, 136.4)]; *m/z* 344 (M^+).

Compound **24** as a colourless crystalline solid, m.p. 166–173 °C; ν_{max}(KBr)/cm^{-1} 3030, 1590, 1480, 1440, 1300, 1160, 1100, 1000. 900, 810 and 680; δ_H(90 MHz; $CDCl_3$) 4.13–4.32 (1 H, m, CH), 4.89–5.08 (2 H, m, =CH_2), 6.02–6.13 (3 H, m, C*H*CH, C*H*=CH_2) and 7.13–7.95 (15 H, m, ArH); δ_C(22.63 MHz; $CDCl_3$) 52.4 (d, $^1J_{PC}$ 65.3, CH) and 117.0–136.6 [ArCs and *C*H=*C*H, *C*H=*C*H (117.0, 127.1, 127.1, 128.2, 128.5, 128.6, 128.7, 128.9, 129.7, 129.9, 131.0, 131.5, 131.8, 132.1, 135.1, 135.6, 136.5, 136.6)]; *m/z* 344 (M^+) (Found: M^+, 344.1350. $C_{23}H_{21}NOP$ requires M^+, 344.1329).

Synthesis of P-*Benzyl*-N,N-*diisopropylphosphonamidic Chloride* **7**.—A dichloro(diisopropylamino)phosphine (4.33 g, 21.40 mmol) solution in anhydrous dichloromethane (15 cm^3) was added to a stirred solution of aluminium chloride (anhydrous; 2.85 g, 21.40 mmol) in anhydrous dichloromethane (15 cm^3) under nitrogen at −78 °C. The mixture was allowed to warm to room temperature over 1 h. Then a solution of benzyl alcohol (1.16 g, 10.7 mmol) in anhydrous dichloromethane (15 cm^3) was added and the mixture stirred for an additional 1 h at room temperature. The mixture was then quenched with water (20 cm^3) and extracted with dichloromethane (30 cm^3 × 3). The combined organic extracts were washed with brine (30 cm^3) and then dried over Na_2SO_4. Purification by chromatography on silica gel eluting with EtOAc–hexane (0:1–1:3) and removal of solvent under reduced pressure gave a solid which was recrystallized from hexane to give the title compound **7** as a colourless crystalline solid in 41% (1.21 g, 4.42 mmol) yield.

Compound **7**: m.p. 69–70 °C; ν_{max}(KBr)/cm^{-1} 3040 [CH(Ph)], 2940, 1600, 1585, 1500, 1450, 1410, 1370, 1245 (P=O), 1020, 990, 770 and 695 [CH(Ph)]; δ_H(90 MHz; $CDCl_3$) 1.04 (6 H, d, *J* 6.8, NCCH$_3$), 1.34 (6 H, d, *J* 6.7, NCCH$_3$), 3.24–3.69 (4 H, m, PCH_2, NCH) and 7.24–7.35 (5 H, m, Ph); δ_C(22.63 MHz; $CDCl_3$) 21.5 (d, $^3J_{PC}$ 2.4, NCCH$_3$), 22.6 (d, $^3J_{PC}$ 4.4, NCCH$_3$), 44.1 (d, $^1J_{PC}$ 114.3, PCH_2), 47.6 (d, $^2J_{PC}$ 3.4, ArC-1C) and 127.4–131.3 (ArCs) (Found: M^+, 273.1055. $C_{16}H_{23}ClNOP$ requires M^+, 273.1048). Compound **7** was also obtained from the reaction of dibenzyl ether (1.00 g, 5.04 mmol) with dichloro(diisopropylamino)phosphine (2.04 g, 10.08 mmol), aluminium chloride (anhydrous; 1.35 g, 10.08 mmol) in 44% (0.61 g, 2.22 mmol) yield.

X-Ray Structure Analysis of Compound (S*,S*)-**3a**.—Suitable single crystals of compound (*S**,*S**)-**3c** were obtained by recrystallization from EtOAc–hexane. Initial lattice parameters were obtained from least-squares fits to 25 reflections, 20.45 < 2θ < 30.18°, accurately centred on a Rigaku AFC5S diffractometer and refined subsequently using higher angle data.

Crystal data for (S*,S*)-**3a**. $C_{16}H_{23}ClNOP$, M_r = 311.79, orthorhombic space group Pb_{ca} (No. 61), *a* = 17.289(9), *b* = 17.312(7), *c* = 11.915(6) Å, *U* = 3566(3) Å^3, D_c = 1.161 g cm^{-3}, *Z* = 8, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 2.97 cm^{-1}.

Totals of 3844 reflections were collected at 20 °C, using the ω–2θ scan technique to a maximum 2θ value of 55.0°. Data sets were corrected for Lorentz and polarization effects. The structure was solved by direct methods using 767 reflections with $I > 3\sigma(I)$. The final residuals were R = 0.087 and R_w = 0.095.

X-Ray Structure Analysis of Compound (S*,R*)-**3a**.—Suitable single crystals of compound (*S**,*R**)-**3a** were obtained by recrystallization from EtOAc–hexane. Initial lattice parameters were obtained from least-squares fits to 25 reflections, 35.29 < 2θ < 39.07°, accurately centred on a Rigaku AFC5S diffractometer and refined subsequently using higher angle data.

Crystal data for (S*,R*)-**3a**. $C_{16}H_{23}ClNOP$, M_r = 311.79, monoclinic space group $P2_{1/a}$ (No. 14), *a* = 12.372(4), *b* = 8.760(6), *c* = 16.012(4) Å, β = 94.65(2)°, *U* = 1730(1) Å^3, D_c = 1.197 g cm^{-3}, *Z* = 4, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 3.06 cm^{-1}.

Totals of 4429 and 4240 unique reflections were collected at 20 °C, using the ω–2θ scan technique to a maximum 2θ value of 55.0°. Data sets were corrected for Lorentz and polarization effects. No absorption correction was necessary for this compound. The structure was solved by direct methods using 1714 reflections with $I > 3\sigma(I)$. The final residuals were R = 0.051 and R_w = 0.072.

Atomic coordinates, bond lengths and angles, and thermal parameters for compounds (*S**,*S**)- and (*S**,*R**)-**3a** have been deposited at the Cambridge Crystallographic Data Centre.†

† For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

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